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Influence of substrate-film reactions on YBCO grown by fluorine-free MOD route

Y. Zhao, X. Tang, W. Wu, J.-C. Grivel

***Abstract*—Recently, fluorine-free metal organic deposition routes (FF-MOD) for growth of YBCO superconducting films have attracted increased attentions. In this work, a comparison study was performed on the YBCO-Ag superconducting thin films deposited on two types substrates, $LaAlO_3$ and CSD-$Ce_{0.9}La_{0.1}O_{2-y}$(CLO)/YSZ respectively. Although conventional TFA-MOD derived YBCO films exhibit high performance on both substrates, the results vary when using the FF-MOD precursor. SEM and XRD results reveal that *c*-axis and *a/b* axis orientations co-exist in the YBCO-Ag films grown on the CSD-CLO/YSZ substrate deposited by the FF-MOD route, while the $BaCeO_3$ by-product is a dominating phase in the fully reacted film. Based on the structural analysis of the partially converted films, we found that interfacial reactions between the film and the CLO cap layer play an essential role on the epitaxial growth of YBCO-Ag films from the FF-MOD solution. Because of the different chemical reaction path compared to conventional TFA-MOD routes, it seems that the polycrystalline $BaCeO_3$ formation takes place prior to the YBCO-Ag epitaxial growth associated with the melting process, which results in structural deterioration at high growth temperatures and therefore no superconductivity. This study indicates the necessity of further reducing the nucleation temperature of YBCO films processed by FF-MOD routes.**

***Index Terms*—YBCO films; all-chemical-solution route; interface reaction; fluorine-free solution.**

I. Introduction

RAPID development of second-generation high-temperature superconductors (2G HTS, REBCO-based coated conductors) holds promise for a revolution in emerging energy-related applications. The main challenges in material science focus on further improvements in the performance of 2G HTS wires through low-cost manufacture routes. Compared with physical deposition approaches, chemical solution deposition (CSD) processes, which enable operation under normal or low-vacuum conditions have received less attention. Chemical deposition routes have the potential for reaching lower price targets considering both the lower capital investments and relatively higher growth rates of the films. Very recently, two world-leading 2G-HTS tape manufacturers working on solution-based production technology, American superconductor company in US and BASF Corporation in Germany, will jointly develop an advanced CSD process [1], implying a great potential for this technique for industrialization.

In the all-CSD routes for 2G HTS wires manufacture, the cap layer (defined as the buffer layer close to the superconducting layer) plays an essential role on the nucleation of the YBCO layer, and consequently has a strong influence on its superconducting performance. In our previous study, we proposed and developed La doped CeO_2 ($Ce_{0.9}La_{0.1}O_{2-y}$, CLO) as a cap layer for an all-chemical derived coated conductors' configuration [2]. A YBCO layer prepared from a low-fluorine MOD (LF-MOD) route was grown on a CLO buffered yttrium stabilized ZrO_2 (YSZ) template and exhibited high performance (>3 MA/cm^2, at 77 K, *sf*) comparable with that of films grown on single crystalline $LaAlO_3$ (LAO) by the same route [3]. Parallelly, a series of solution precursors with various amount of fluorine have been developed in our group [4-6]. Almost all of the precursors enable obatining high performance YBCO films on LAO single crystals. Unlike in conventional TFA-MOD routes, the nucleation and growth of YBCO is governed by evolution of the intermediate $BaCO_3$ phase in the FF-MOD routes. One possible conversion mechanism based on solid-state reaction experiments is that $BaCO_3$ reacts with CuO to generate the $BaCuO_2$ phase, followed by further reacting with CuO to form a transition liquid phase. YBCO is eventually formed through reaction of the liquid phase and Y_2O_3 [7, 8]. Therefore, the different YBCO conversion paths certainly result in different growth conditions, e.g. normally a higher growth temperature related to the melting process is critical in the FF-MOD routes. Recently, a novel silver assisted fluorine-free metal organic deposition (SAFF-MOD) route has been proposed to reduce the growth temperature and further enhance the J_c values [6]. With help of silver addition the incongruent melting temperature of YBCO is lowered, and a smooth and dense morphology is observed on the YBCO film surface at a growth temperature as low as 760 ^{o}C, leading to improved intergranular conductivity. A high J_c of 4.6 MA/cm^2 at at 77 K, *sf* was obtained in a 200 nm thick YBCO-Ag thin film with optimal amount of Ag (10 wt.%) on LAO substrates.

In this work, we employed the SAFF-MOD route to deposit YBCO-Ag films on CSD-CLO/YSZ substrates to examine their compatibility. The fully reacted and partially reacted films were characterized by means of X-ray diffractometer (XRD) and scanning electron microscopy (SEM). A comparison study was performed on the YBCO-Ag superconducting thin films deposited on two types substrates, LAO and CSD-CLO/YSZ, respectively. As a result, the possible chemical reaction sequence for SAFF-MOD YBCO on CSD-CLO/YSZ was proposed according to the structural evolution analysis.

II. Experimental Details

The deposition of the CLO films and the YBCO-Ag films by chemical solution routes were published previously [2, 6]. The CLO films were prepared using a propionates-based metal-organic solution, while the YBCO-Ag films were prepared by using the SAFF-MOD precursor. The SAFF-

MOD precursor was synthesized by mixing stoichiometric amounts (1:2:3) of Y, Ba and Cu acetates, i.e., $Y(CH_3COO)_3 \cdot xH_2O$ (Purity 99.9%, Sigma-Aldrich), $Ba(CH_3COO)_2$ (Purity 99%, Alfa-Aesar), $Cu(CH_3COO)_2 \cdot H_2O$ (Purity 98%, Alfa-Aesar) and 10% weight of $AgNO_3$ (Alfa Aesar) into in a mixture of propionic acid and ammonia (volume ratio of 3:1). After one hour stiring at 80 ^oC on a heating plate, the solution became clear blue without any precipitation, followed by removing all the extra solvent by an evaporator. Finally, the gels were dissolved in methanol (Alfa Aesar), to yield a homogeneous solution with a total metal concentration (Y, Ba and Cu, regardless of Ag) of 1.5 mol/L.

The precursor solutions were deposited by spin coating at a rotation speed of 3000 rpm, under which conditions the film thicknesses after full process are around 200 nm. Two single crystals served as substrates, *i.e.* 5 mm×5 mm (001) LAO single crystals (CrysTec GmbH) and home-made CLO buffered YSZ single crystals (YSZ from CrysTec GmbH). A typical three-step heat treatment process including pyrolysis, sintering and oxygenation was performed in an atmosphere-controlled tubular furnace for processing all the films. Firstly, the coated films were directly inserted into the furnace pre-heated at about 100 ^oC in order to avoid water absorption at ambient conditions, and heating up to 470 ^oC with a ramping rate of 10 ^oC /min in a humid oxygen flow with a room temperature dew point. Secondly, the sintering process was performed at 800 ^oC for 2 hours with a heating ramp of 20 ^oC/min in dry forming gas flow (Ar/300 ppm O_2). Finally, the samples were furnace-cooled down to 450 ^oC, with holding for several hours in pure oxygen.

The phase and global texture of the films were examined by means of XRD with Cu K_a radiation in a four-circle diffractometer (Rigaku, smartlab). The reciprocal space map is plotted based on θ-2θ scans at several omega positions. The morphology of the films was observed in a SEM equipped with an inlens detector (Zeiss Supra 35). The superconducting transition temperature (T_c) was determined by AC susceptibility measurements with an AC field amplitude of 0.1 mT and frequency of 21 Hz. The critical current densities, J_c, were determined by VSM and calculated based on the Bean model using the opening of the hysteresis loops obtained under a magnetic field applied perpendicular to the plane of the films.

III. Results and Discussions

A. Quality of the CLO buffer layer grown on the YSZ substrate

First, the quality of the CLO cap layer deposited on the YSZ single crystals was examined by XRD and AFM techniques. As shown in Fig. 1 inset, the sharp diffraction spot of the CLO (111) reflection below the YSZ (111) reflection demonstrates the cube-on-cube epitaxial relationship between the substrate and the film. The AFM morphology scan (no shown) shows that the surface roughness is as low as 1 nm over 1 μm×1 μm area. Furthermore, the typical low-TFA MOD solution was employed for growth of the YBCO film on top. Previous results show that the CLO cap layer is nearly consumed completely during the YBCO growth, even at a deposition temperature as low as 740 ^oC [3]. However, sharp in-plane and out-of-plane texture and excellent superconducting properties were still achieved in the YBCO film. The typical double logarithmic plots of J_c vs. magnetic field B measured at 77 K for a YBCO/CLO/YSZ film is plotted in Fig. 1, which is comparable with that of films deposited on LAO substrate [3]. This is indicative of the high quality of the CLO cap layer and good compatibility between the CSD-CLO and the low TFA-MOD YBCO films.

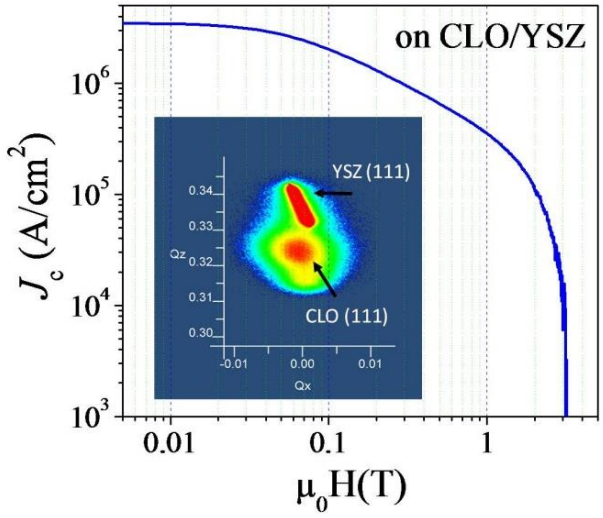

Fig. 1. Plot is dependence of J_c on the applied magnetic field at 77 K for LF-MOD YBCO on CSD-CLO/YSZ, and the inset shows the XRD reciprocal space map around CLO (111) reciprocal lattice piont for CSD-CLO on YSZ substrate.

B. Superconductivity and structure characterization of the FF-MOD YBCO-Ag films on the CLO/YSZ and LAO substrates

After examining the quality of the CSD-CLO cap layer, a series of specimen were prepared and compared with each other in terms of superconducting properties in order to investigate the influence of the substrates during the YBCO growth using various precursors. All the synthesis route, type of substrates as well as key superconducting properties are summarized in Table 1. It can be seen that the low TFA-MOD route enables reaching high-performance YBCO films on either LAO or CLO/YSZ substrates. Furthermore, the growth temperature window is relatively broad, which is in agreement with the results published by other researchers [9]. In the case of the SAFF-MOD route, the YBCO films also exhibit superior crystal structures and excellent superconducting performance on LAO substrates, as evidenced by the high transition temperature of 90 K, small transition width of less than 1 K, and high J_c values of 3-4 MA/cm^2 at 77 K, *sf.* [6]. Surprisingly, when applying the SAFF-MOD route on the CLO/YSZ substrate, no superconductivity is found in the film processed under the investigated conditions.

To understand the difference of the superconducting properties of the YBCO deposited on the CLO/YSZ and LAO substrates, the films were characterized by XRD and SEM, as shown in Figs. 2 and 3. From the XRD θ-2θ scans, we noticed serious CLO-YBCO interfacial reactions, as evidenced by the presence of a large amount of $BaCeO_3$ phase. Although no intermediate phases are observed in the fully processed film, the presence of *a/b* grains and randomly orientated (103)

grains is significant, i.e., the intensity of the YBCO (200) diffraction peak is almost as strong as that of YBCO (006) in the film deposited on the CLO/YSZ substrate. As a result, the *c*-axis texture in the YBCO film deposited on the CLO/YSZ substrate is much weaker than that on the LAO substrate. In the SEM images, it is seen that both films are rather dense without any pin-holes, which is connected with the existence of a transient liquid phase during the SAFF process. However, compared with the YBCO-Ag grown directly on a LAO substrate, large amount of elongated grains can be seen in the film deposited on the CLO/YSZ substrate, being an indication of *a/b* grains, in agreement with the XRD phase analysis. Because of the presence of $BaCeO_3$ impurities and grains with undesirable orientations, it is easy to understand that no superconducting transition was observed on the CLO/YSZ substrate.

TABLE I
SUPERCONDUCTING PROPERTIES OF YBCO FILMS DEPOSITED USING DIFFERENT PRECURSORS ON DIFFERENT SUBSTRATES

Substrate	Precursor	T_c (K)	J_c (at 77 K , sf)	T_{growth}
$LaAlO_3$	Low TFA	91	~3-5 MA/cm^2	broad
CLO/YSZ	Low TFA	89	~3 MA/cm^2	740 °C
CLO/YSZ	Low TFA	91	~3 MA/cm^2	770 °C
$LaAlO_3$	SAFF	90	~3-4 MA/cm^2	800 °C
CLO/YSZ	SAFF	/	/	800 °C-740 °C

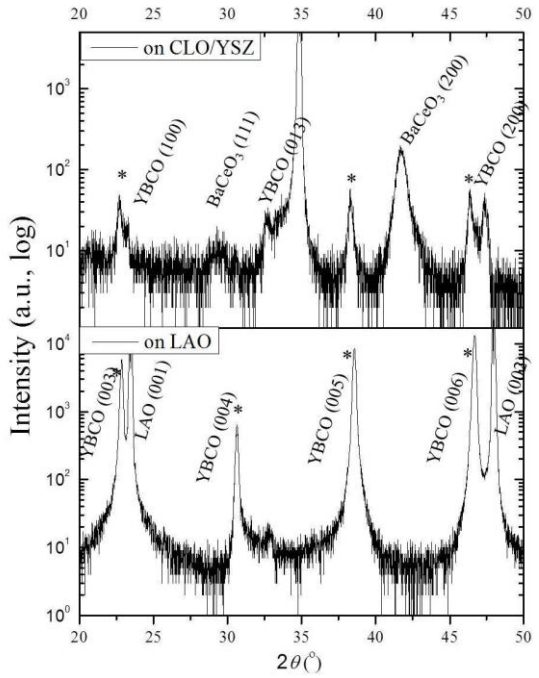

Fig.2. XRD patterns of the SAFF derived YBCO-Ag films. Upper panel is on the CLO/YSZ substrate, and the lower panel is on the LAO substrate. Both films are fully processed. The peaks marked with asterisk are the YBCO (*00l*) reflections.

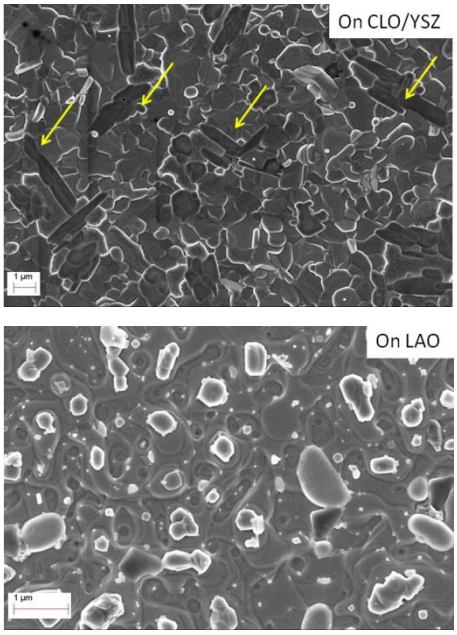

Fig. 3. SEM images of the YBCO-Ag films grown on the CLO/YSZ (upper) and on the LAO substrate (lower), where the arrows in the upper panel point to the enlongated grains.

C. Structure evolution of the SAFF-MOD YBCO-Ag films deposited on CLO/YSZ

To shed light on the structural difference between the YBCO films deposited on the CLO/YSZ and LAO substrates, partially reacted SAFF-MOD YBCO-Ag films on the CLO/YSZ were prepared by quenching the samples at different conversion temperatures without dwell time. From the XRD θ-2θ scans shown in Fig. 4, it can be seen that at low sintering temperature (e.g., 690 °C) the $BaCeO_3$ already formed, while the randomly orientated grains (YBCO (103)) co-exist with *c*-axis orientated grains. With increasing the sintering temperatures, the intensity of the YBCO (103) reflection remains unchanged, and the *a/b* axis grains appear and become stronger. Further increasing the temperatures lead to competitive growth of (00*l*) and (*h*00) grains, and the $BaCeO_3$ (200) peak develops rapidly. As a result, the intensities of the YBCO (006) and (200) peaks are comparable, and $BaCeO_3$ (200) became the most intense peaks at the fully reacted stage.

Compared with the nucleation and growth processes occurring in the SAFF-YBCO films on the LAO substrates or the TFA-YBCO films on the CLO/YSZ substrates, we should notice the following differences. i) Evolution of the YBCO grains with undesirable orientation: In the case of SAFF-YBCO films on LAO substrates, at the small amount of randomly orientated grains also show up at early stage of nucleation, but this is followed by their rapid consumption by (00*l*) axis grains in the presence of the molten phase at high growth temperatures. Due to this growth advantage, development of both the (*h*00) and (103) grains is suppressed when the growth proceeds. However, in the case of using CLO/YSZ substrates, it seems that the grains with secondary orientations especially *a/b* axis grains develop together with the *c*-axis grains. Unlike the process on the LAO substrate, the large *a/b* axis grains could not be consumed even when

reaching the melting temperature. Consequently, several texture components coexist in the fully reacted films. ii) Evolution of the $BaCeO_3$ phase: It is known that at the CeO_2-YBCO interface reaction is inevitable. The main products of this interfacial reaction are Y_2BaCuO_5, $BaCeO_3$ and CuO, and the extent of the reaction is strongly dependent on the sintering process of the YBCO film [10]. The formation of $BaCeO_3$ has little negative influence on the epitaxial growth in the TFA-YBCO on CLO/YSZ even at higher temperatures, which is associated with the order of YBCO epitaxial growth and interfacial reactions. Moreover, $BaCeO_3$ phase does not develop with increasing the annealing temperature in the TFA-YBCO-CLO/YSZ constitution according to the XRD analysis. In contrast, epitaxial growth in the SAFF-MOD route is accomplished by re-organization during the melting process at high temperature. Therefore, we suspect that the top of the cap layer is already from by polycrystalline $BaCeO_3$, which could not provide texture template for YBCO growth. However, we notice that Yamaguchi, et.al. reported that high J_c values can be obtained on the FF-MOD YBCO films deposited on CeO_2 cap layers prepared by vacuum evaporation technique [11]. This difference implies that the poor chemical compatibility of the CSD-CLO layer with the SAFF-MOD routes might be related to the microstructure features generated by the CSD processes.

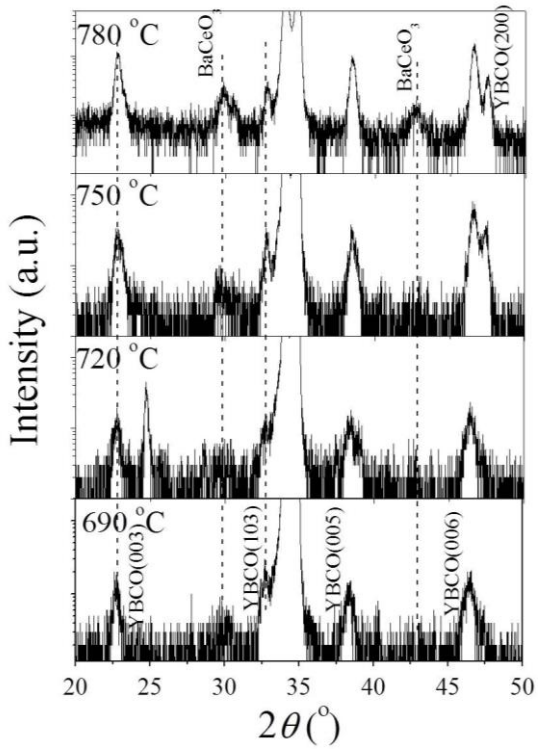

Fig.4. XRD patterns of the partially reacted SAFF-MOD YBCO-Ag films on the CLO/YSZ quenched from different temperatures without dwell time.

IV. Conclusion

We compared YBCO-Ag superconducting thin films deposited on two types of substrates, $LaAlO_3$ and CLO/YSZ using the SAFF-MOD route. The SEM and XRD results show that the film grown on a CLO/YSZ substrate exhibits a large amount of *a/b* axis grains. The results reveal that the interface reactions between the YBCO-Ag films and the CLO cap layer play an essential role on the nucleation and growth of YBCO-Ag films from the SAFF solution. High melting temperature for the epitaxial structure re-construction and serious interface reactions seem to be the main explanations for the poor superconducting performance when using CLO/YSZ as substrate. Further investigations of the compatibility of the CSD-buffer layers for FF-MOD YBCO films are obviously needed to solve these issues.

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